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Bureau of Mines Report of Investigations/1981

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By D. A. Stanley, B. J. Scheiner, and P. Brown

UNITED STATES DEPARTMENT OF THE INTERIOR

I 28.23:

Report of Investigations 8535

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James G. Watt, Secretary
BUREAU OF MINES

Research at the Tuscaloosa Research Center is carried out under a memorandum of agreement between the Bureau of Mines, U.S. Department of the Interior, and the University of Alabama.

This publication has been cataloged as follows:

Stanley, Donald A

Treatment of Florida surface waters for use in phosphate beneficiation.

(Report of investigations ; 8535)
Bibliography: p. 10.
Supt. of Docs. no.: I 28.23:8535.

1. Water–Purification–Flocculation. 2. Water–Purification–Filtration. 3. Phosphate indsutry–Florida–Equipment and supplies. I. Scheiner, Bernard J., joint author. II. Brown, Pat M., joint author. III. Title. IV. Series: United States. Bureau of Mines. Report of investigations ; 8535.

TN23.U43 [TD455] 622s [661'.43] 80-606882

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TREATMENT OF FLORIDA SURFACE WATERS FOR USE IN PHOSPHATE BENEFICIATION

by

D. A. Stanley,[1] B. J. Scheiner,[2] and P. Brown[3]

ABSTRACT

The Bureau of Mines conducted laboratory-scale experiments to determine whether or not surface waters with a high organic content could be purified sufficiently to be used to replace the natural high-quality deep well water currently being used in the silica flotation step of phosphate rock beneficiation. Waters abundant in organic matter were collected from two central Florida streams, flocculated with a cationic polyethylenimine polymer, and processed in a sand filter. This treatment removed most of the organic materials from the water. Untreated surface water, treated surface water, and distilled water were used to compare the flotation response of the acid insolubles in an amine flotation circuit. Surface water treated with PEI-1000 was shown to be as effective as distilled water for the acid-insoluble-flotation step.

Flocculation and filtration can therefore produce water suitable for amine flotation of quartz, which would permit substitution of surface water for deep well water.

INTRODUCTION

In response to competition for water by other users, the phosphate mining industry has reduced its total water use from 317 MMgpd in 1970 to 243 MMgpd in 1975, principally by recycling. Water is recycled by allowing process water containing waste clays and other particulate matter to settle in large impoundments (8).[4] However, owing to the nature of these wastes, which are slow to settle, losses of 5 tons of water per ton of phosphate rock produced are common.

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[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Lost water is generally replaced by deep well pumping from the Floridian aquifer. The requirements for deep well water by agricultural, industrial, and governmental entities are expected to more than double in the 1980's (5). Therefore, an alternative to deep well water may be needed. A potential source of supply is surface water (3); however, humic products discolor many central Florida surface waters. These humic substances are negatively charged macromolecules that interfere with the flotation beneficiation process so that surface water cannot be used in the beneficiation flowsheet (4). The associated color is a product of the bacterial breakdown of organic matter, principally lignin, and can be used to determine the organic content of the water. The result is a wide range of compounds of generally similar properties with numerous carboxyl, phenol, and hydroxyl groups in the molecules. These compounds have been divided into fulvic, hymatomelanic, and humic acids based on differences in solubility. Fulvic acid is reported to have molecular weights of 200 to 300, while humic acid has molecular weights of 700 to 26,000 (1).

Certain cationic organic polymers such as the polyethylenimine type react chemically with humic materials and have been used on a laboratory scale to flocculate these products from waters (2). Polyethylenimine polymers are highly branched polyamines containing primary, secondary, and tertiary amino nitrogens and are produced by the acid-catalyzed polymerization of ethylenimene, C_2NH_5. When polyethylenimines are dissolved in water, the amino nitrogens react to form positively charged amino groups, which react with the humic material to form destabilized particles that subsequently accumulated into large agglomerates that can be filtered.

The technology of color removal has been developed for municipal water supplies (7). This technology generally is based on flocculation by aluminum or iron salts rather than organic materials. The flocs are removed by rapid sand filtration. These water purification systems operate on less highly colored water than that available from streams in central Florida. With increase in organic material, the aluminum or iron salts systems can become cumbersome.

As part of the Bureau of Mines mineral resources technology research program, an investigation was made to determine whether a simple method for treating Florida surface waters to make them amenable for beneficiating phosphate ores could be developed. This report describes the results of tests made to determine if polyethylenimine could be used to remove organic substances from two Florida surface waters and to determine if the treated water was acceptable for amine flotation of acid insolubles from phosphate concentrates.

MATERIAL AND PROCEDURE

The polyethylenimine (PEI) used in this study was marketed by Dow Chemical Co. under the trade name of PEI-1000[5] and has a molecular weight of 50,000 to 100,000. Water samples were obtained from Oak Creek and Horse Creek

[5]Reference to specific trade names does not imply endorsement by the Bureau of Mines.

located in Polk County, the center of the phosphate-producing area of central Florida. The water as received was brown in color and contained no detectable turbidity. The organic content of the waters was determined in Pt-Co units using a Hellige Aqua Tester. This instrument compares the color of water to that of a series of standard glass disks. The color of the Horse Creek and Oak Creek waters was 300 Pt-Co units.

Turbidity measurements were made using a Hach Model 2100 turbidimeter and are reported in NTU (nephelometric turbidity units).

Initial screening tests were conducted by adding 100 ml of the colored water to a series of beakers. Varying amounts of PEI were then added to each beaker, and the flocculated material was allowed to settle for 1 hour before the turbidity of the supernate was measured. This data provided an initial estimate of the amount of polymer needed for removal of color.

In semicontinuous bench-scale tests a polymer solution was pumped into a mixing chamber. Colored water was then pumped into the chamber to allow contact of the polymer and colloidal particles. Figure 1 shows the finished apparatus. A sand filter was made by packing a 2-inch plastic column to a depth of 10 inches with a minus 30- plus 40-mesh Ottawa sand. In other experiments the mixing chamber was eliminated, and the polymer solution was fed directly into the colored water stream.

During operation the pressure was monitored by a gage placed between the pumps and the filter bed. When the pressure reached a preselected value of 2 psi, the filter bed was fluidized by forcing a flow of clean water back through the bed. This removed trapped material and cleaned the bed for reuse. Prior to operation, the bed was conditioned by passing a small amount of concentrated PEI solution through it.

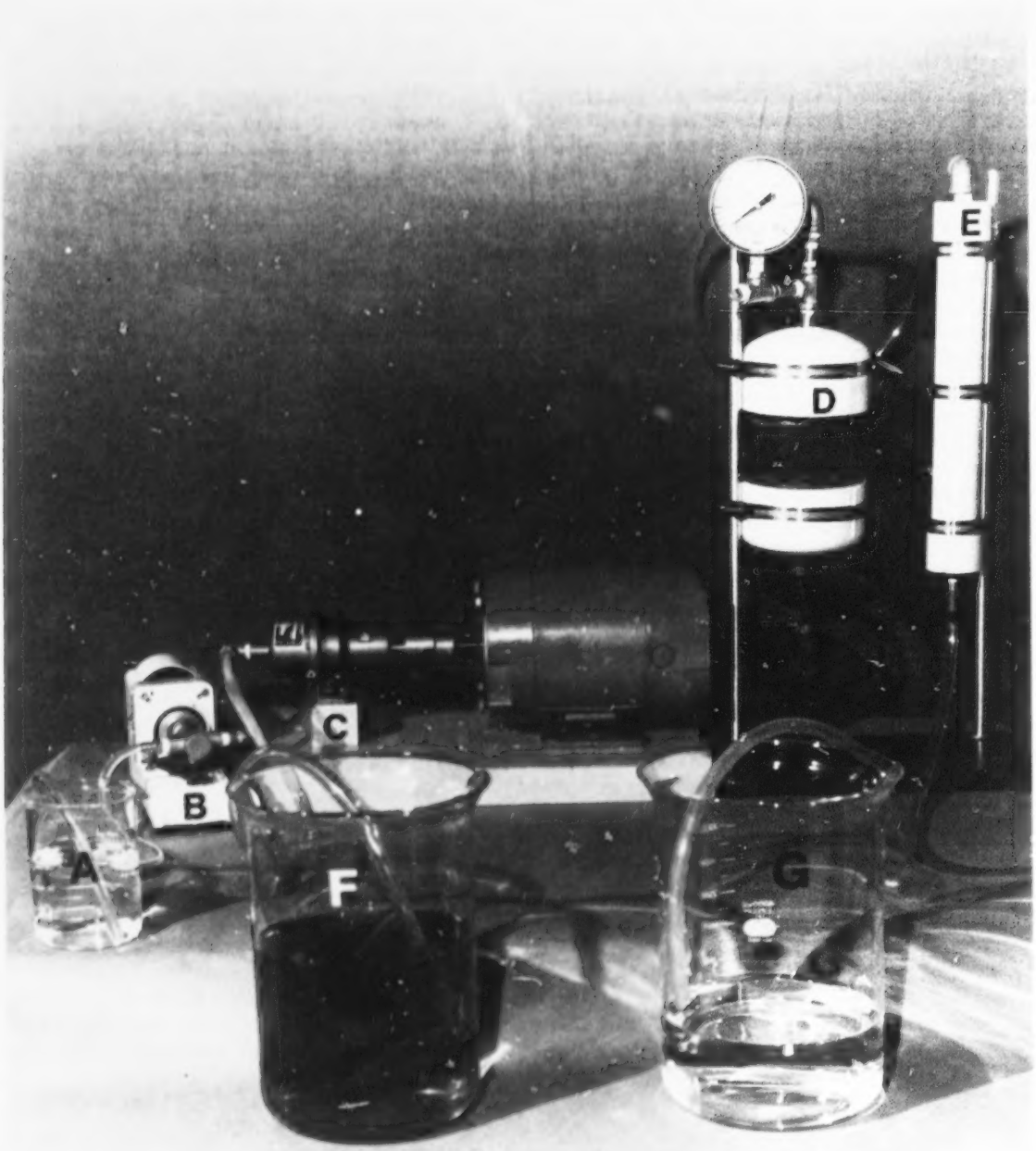

FIGURE 1. - Sand filter and associated equipment used to remove color from water. A, Polymer solution; B, polymer solution pump; C, water pump; D, mixing chamber; E, sand filter; F, colored water; G, product water reservoir.

RESULTS AND DISCUSSION

Treatment of Horse Creek Water

A series of continuous tests was conducted in which Horse Creek water was treated with PEI and filtered in the sand filter at a rate of 4 gal/sq ft/min. Figure 2 shows the results of these tests. Maximum color removal was observed in the range of 25 to 40 mg of PEI per liter. Since the amount of organic material is proportional to color, this is also the optimum range for removal of organic material. At 40 mg/l the amount of residual color increased, indicating charge reversal and restabilization of the colloid. During the filtration tests, the pressure increased in the sand filter owing to clogging of the filter with the flocculated material. This necessitated frequent backflushing of the system.

To overcome the need for frequent backflushing of the sand filter, a series of tests was made in which PEI was added to the water and stirred for a

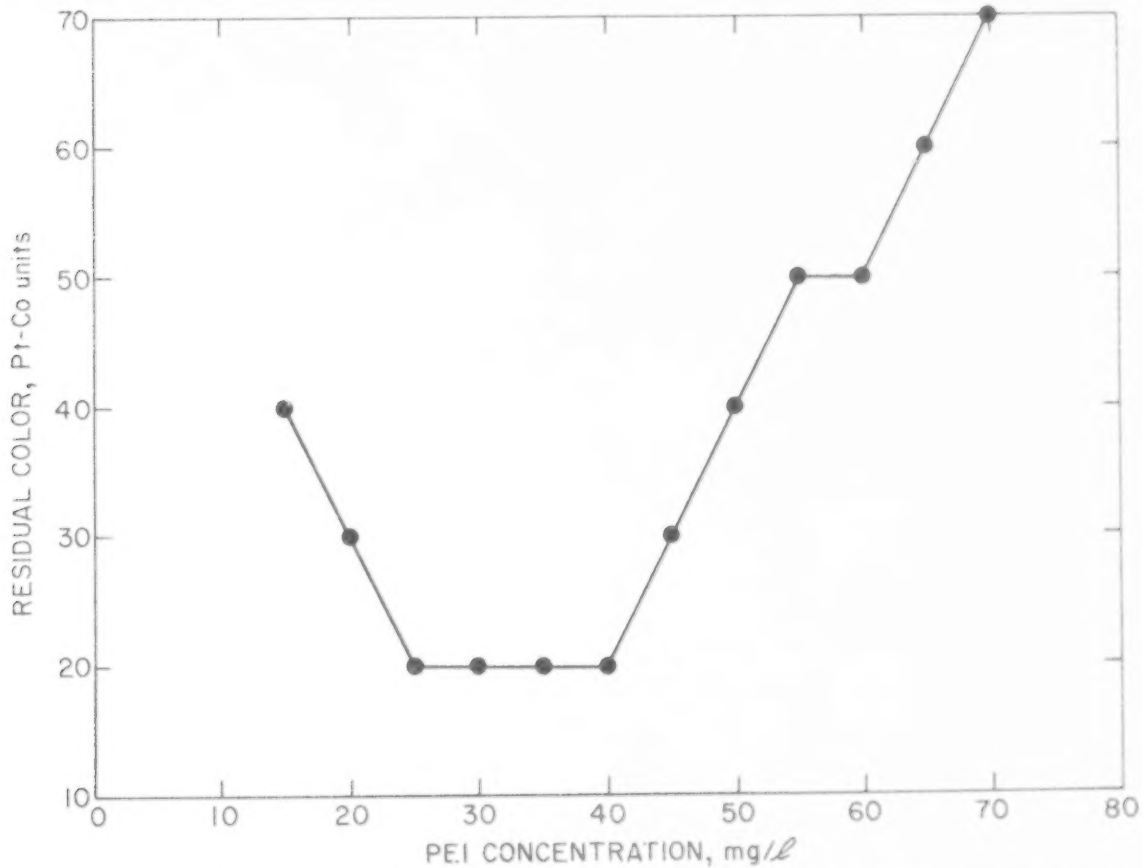

FIGURE 2. - Effect of PEI addition followed by filtration on organic content of Horse Creek water.

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given period to establish an optimum stirring rate to form large flocs which settled rapidly. Table 1 shows the results of tests using Horse Creek water treated with 20 mg/l of PEI in an agitated vessel. In the table the stirring rate is expressed in terms of tip speed of 2.5-inch-diameter stirrer.

TABLE 1. - Effect of stirring on turbidity for Horse Creek water treated with PEI

Time, min	Turbidity, NTU			
	Limited stirring	Tip speed of 34 ft/min	Tip speed of 88 ft/min	Tip speed of 200 ft/min
0.....	52	48	45	43
10.....	53	39	17	38
20.....	52	31	13	22
30.....	52	27	11	17
40.....	51	25	10	14
50.....	49	25	10	13
60.....	46	23	ND	12
70.....	44	22	ND	12
80.....	38	22	ND	ND
90.....	35	ND	ND	ND
100.....	33	ND	ND	ND
110.....	28	ND	ND	ND
120.....	27.5	ND	ND	ND
130.....	25+	ND	ND	ND
140.....	26	ND	ND	ND

ND Not determined.

The series labeled "limited stirring" was conducted by adding the PEI and stirring with a glass rod to sufficiently mix the PEI with the solution. In the other tests, the PEI was added and stirred at various tip speeds for 5 minutes. The turbidity was then measured at 10-minute intervals to determine the amount of settling. When PEI is added to the solution, the organic material and PEI form a precipitate. Turbidity is a measure of the number of particles suspended in the solution. Higher turbidity values relate to smaller flocs that settle slowly. Larger agglomerates that settle rapidly resulted in lower turbidity. The data indicate that a tip speed of 88 ft/min gave a turbidity of 10 after 40 minutes of settling. Therefore, for the water and conditions tested, the organic PEI agglomerates settled faster for the 88-ft/min series. It should be noted that the optimum stirring speed used is dependent on vessel size, configuration of vessel, and tip speed of stirrer blade; for the mixing system used, 88 ft/min was near optimum. A test was conducted on Horse Creek water where 20 mg of PEI per liter was added and stirred for 40 minutes at 88 ft/min. The material was then filtered in the sand filter at the rate of 4 gal/sq ft/min. No backflushing was required in 4 hours of operation. The residual color was 20 color units.

Treatment of Oak Creek Water

A series of tests was conducted in which Oak Creek water was treated with various amounts of PEI with limited stirring and allowed to stand for 1 hour

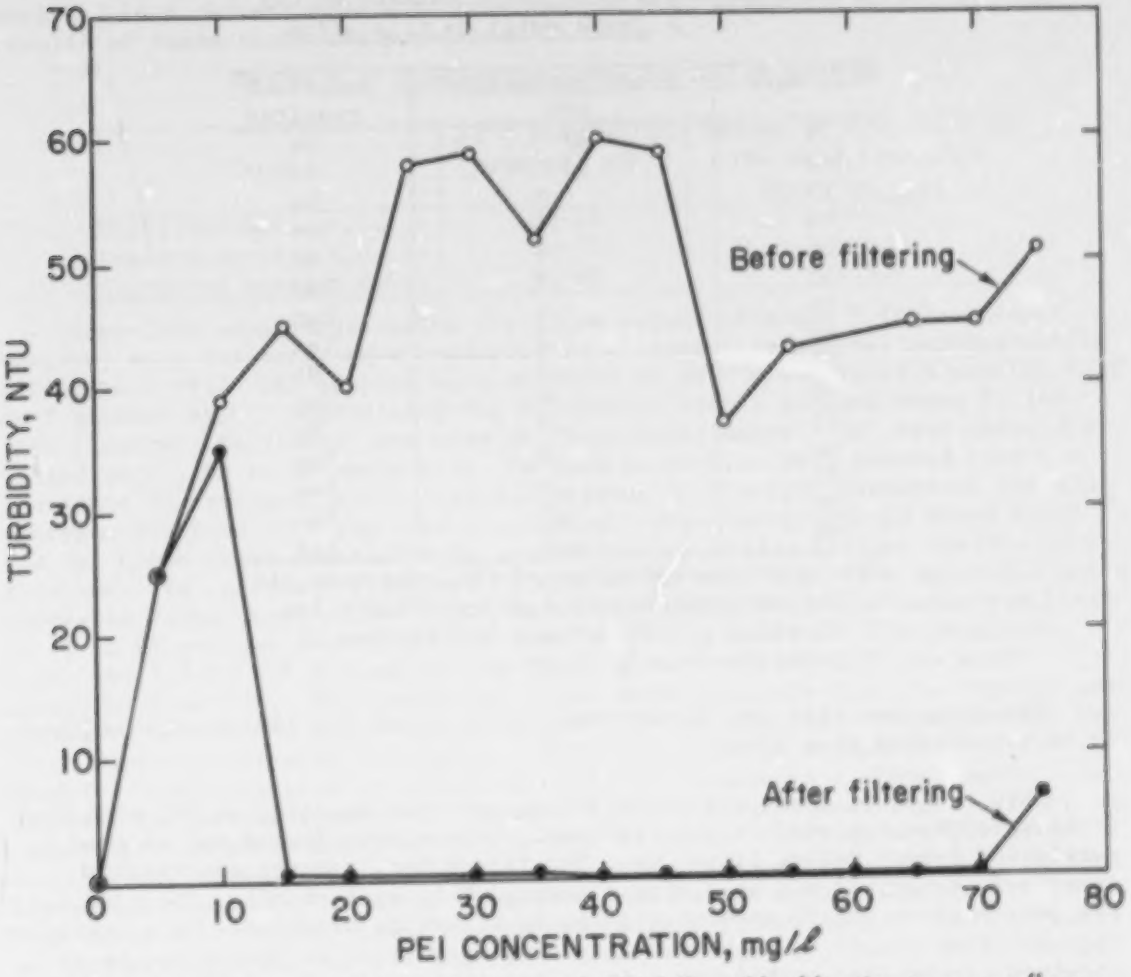

FIGURE 3. - Treatment of Oak Creek water with PEI followed by filtration to remove flocculated organic material.

prior to filtration. The results of the series are shown in figure 3. The turbidity increased to a maximum of 60 NTU's with 40 mg of PEI per liter. Filtration removed essentially all of the turbidity within a dosage range of 15 to 70 mg/1. As previously observed with the Horse Creek water, the pressure on the sand filter would rise above 2 psi and backflushing was required. The results for this series of tests are summarized in table 2.

TABLE 2. - Effect of PEI treatment of Oak Creek water on filtration

PEI, mg/l	Final turbidity, NTU	Backflush[1] required
5	25	No
10	35	No
15	.8	No
20	.6	Yes
25	.8	No
30	.5	Yes
35	.4	Yes
40	.2	Yes
45	.3	No
50	.2	Yes
55	.3	No
60	.2	Yes
65	.2	Yes
70	.3	Yes
75	6.7	Yes

[1]For each concentration of PEI, the sand filter was operated at 4 gal/sq ft/min for 15 minutes. Filter was backflushed if pressure exceeded 2 psi.

The data show that the filter operated in total for 240 minutes and had to be backflushed nine times.

This series of tests was repeated, except that settling of PEI with Oak Creek water was included in the treatment. Flocs were formed and allowed to settle for 1 hour before filtering. The filter bed from the experiments described in table 2 was used with a dosage of 15 mg/l of PEI. The sand filter was operated for 75 minutes with no backflushing required. This indicates that stirring of PEI with the water and settling prior to filtration is required if frequent backflushing is to be eliminated. The color removal was better than 90 percent.

Flotation of Acid Insolubles From Phosphate Concentrates With Treated Water

Current practice in beneficiation of Florida phosphate matrix includes recovery of coarse pebbles by screening and flotation of the plus 150-mesh fraction with a fatty acid to produce a phosphate concentrate; this concentrate is subsequently refloated with amine as the collector to remove the acid-insoluble material. In the second flotation step, aquifer water is used. Fresh water is used in this step because recycled water often interferes with the amine flotation. To determine if PEI treatment interfered with the flotation of acid insolubles, a series of flotation experiments was conducted using treated surface water, and the results were compared with data obtained using untreated water and distilled water. An acid-scrubbed and deoiled flotation feed was obtained from an operating Florida concentration facility; it

analyzed 28.6 percent P_2O_5 and 12.86 percent acid-insoluble material. The results of these tests are summarized in table 3.

TABLE 3. - Summary of amine flotation tests

Water	Acid insolubles removed, pct	Amount of P_2O_5 lost to the acid insoluble fraction, pct
Distilled H_2O.....	80-85	1.0-1.5
Treated surface H_2O....	80-85	1.0-1.5
Untreated surface H_2O..	80-88	4.3-6.9

Base-line experiments using distilled water and Armac T (tallow amine acetate) as a collector were conducted in a laboratory mineral separation flotation cell (6). The samples were adjusted to pH 7 with either 5 percent NaOH or 5 percent H_2SO_4, conditioned for 0.5 minute with 1 percent Armac T, and then floated. No frother was used in these experiments. In tests using distilled water, 80 to 85 percent of the acid insolubles were removed from the phosphate concentrate, and 1.0 to 1.5 percent of the P_2O_5 content of the concentrate reported with the acid insolubles. When using treated Horse Creek and Oak Creek water containing 25 or fewer color units, similar results were obtained. In contrast, flotation to remove the acid-insoluble materials using untreated Horse Creek or Oak Creek water containing 300 color units resulted in 80 to 88 percent removal of the acid-insoluble material from phosphate feed, but 4.3 to 6.9 percent of the P_2O_5 values reported with the acid-insoluble fraction. The results of these tests indicate that the organic constituents in surface water result in flotation of phosphate values during the amine flotation of acid insolubles. This flotation of phosphate into the acid-insoluble fraction is important since it represents a significant decrease in overall recovery. For both distilled water and treated water, the upper limit on phosphate lost to the acid-insoluble fraction was 1.5 percent, whereas for retreated water the amount lost was 6.9 percent. This difference represents the amount of total phosphate lost to the acid-insoluble fraction. This means that for distilled and treated water, the phosphate recovery would be 98.5 percent, whereas for untreated water the recovery could be as low as 93.1 percent. This difference would have a tremendous impact on the economics of the phosphate mine. For the conditions tested, the PEI-treated water that has an organic content equal to or less than 25 color units does not increase the loss of P_2O_5 with the acid insolubles when compared with distilled water.

CONCLUSIONS

In bench-scale tests, most of the organic material contained in two surface waters from central Florida was removed, and the resulting water was successfully utilized in the amine flotation of insoluble substance from phosphate concentrate. The procedure giving best results consisted of treating the surface waters with polyethylenimine in an agitated vessel, followed by 1-hour settling of the resulting agglomerates. The agglomerated organic materials were removed from the waters by filtering in a sand filter.

The flotation data indicated that surface waters containing organic material could be treated and used in the amine flotation sequence to remove quartz from a phosphate feed with minimum loss of P_2O_5.

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